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Ab Initio Molecular Orbital Calculations

I. Minimal Basis Calculations on Furan, Pyrrole and 1,2,5-Oxadiazole

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Linear combinations of Gaussian orbitals were contracted to minimal basis sets. The binding energies (B.E.) obtained for the three compounds furan, pyrrole and 1,2,5-oxadiazole are 0.75, 0.84 and 0.26 a.u. respectively. Correlation of these figures and those obtained in related calculations leads to the relationship $(\text{B.E.})_{\text{exp.}} = 0.7347\,(\text{B.E.})_{\text{calc.}} + 633$ (Kcal/mole). The photoelectron spectra of these compounds are extended and correlated with the orbital energies; the π-electron excitations are given by $(\text{I.P.})_{\text{exp.}} = 1.00\,(\text{I.P.})_{\text{calc.}} - 2.20$ eV. Mulliken population analyses give dipole moments in reasonable agreement with experiment.

Linearkombinationen von Gauß-Orbitalen wurden zu minimalen Basissätzen kontrahiert.

Die Bindungsenergien (B.E.) für die drei Komponenten Furan, Pyrrol und 1,2,5-Oxadiazol haben die Werte: 0,75, 0,84 und 0,26 a.u. Setzt man diese Werte zu den berechneten in Beziehung, so erhält man die Gleichung: $(\text{B.E.})_{\text{exp.}} = 0{,}7347\,(\text{B.E.})_{\text{calc.}} + 633$ (Kcal/Mol).

Die Photoelektronenspektren dieser drei Komponenten werden erweitert und mit den Orbitalenergien korreliert; die π-Elektronen-Anregungsenergien werden durch die Beziehung: $(\text{I.P.})_{\text{exp.}} = 1.00\,(\text{I.P.})_{\text{calc.}} - 2{,}20$ eV gegeben. Mulliken-Populations-Analysen ergeben die Dipolmomente in bemerkenswerter Übereinstimmung mit experimentellen Werten.

Recently ab initio calculations have been carried out on molecules of increasing size and it seems probable that the next few years will see calculations of near Hartree-Fock accuracy routinely carried out on molecules with up to about 100 electrons [1]. The availability of computer programs such as IBMOL and POLYATOM etc. [2] assists this process. Following our interest in the structure and reactivity of heterocycles [3] we report our first ab initio calculations for these molecules using a minimal basis, [4–6] with one calculation on furan and 1,2,5-oxadiazole and two on pyrrole; these last calculations used a more recent geometry and a better gaussian set [7] than was used previously; they also enabled us to perform final checks on the IBMOL-4 and IBM 360/50 system under large scale operating conditions, and to link our results to those of the earlier work. In the following paper [8] we report extensions of these calculations to include polarisation orbitals and to discuss in greater detail the photoelectron spectra of these molecules. In the present work we also report details of the exponents and contractions used; they have been used in a variety of calculations that we have performed and will not be detailed in later papers. In order to reduce the number of tables to a minimum, eigenvectors will not be given, but will be supplied on request.

Computational Methods

Calculations on the contraction procedures for the atoms were carried out with the program ATOM-SCF, and for the molecules by A. Veillard's version IBMOL-4 of the program IBMOL. In this version the auxilliary integrals required for the electron repulsion integrals are stored in the core of 512 K bytes. Several of the key routines are written in assembler code, and this also achieves a considerable saving in time over the earlier version IBMOL-2.

Seven *s*-type and three *p*-type gaussian sets [7] for carbon, nitrogen and oxygen (Table 1) were contracted to five for 1*s*, two for 2*s* and three for each 2*p* orbital [cf. Refs. 4–6]; three hydrogen exponents [5] were contracted to one 1*s* function. A comparison of these contracted functions with the Hartree-Fock and the uncontracted sets is given in Table 2; we note in passing that energies quoted for the sets used by Clementi [4, 5] in fact refer to the uncontracted *not* the contracted sets[1], hence the binding energies quoted in Ref. [6] from this data

Table 1. *Orbital exponents and contraction coefficients*

Hydrogen		Carbon		Nitrogen		Oxygen	
Exponent	Coefficient	Exponent	Coefficient	Exponent	Coefficient	Exponent	Coefficient
(1*s*)	(1*s*)	(1*s*)	(1*s*)	(1*s*)	(1*s*)	(1*s*)	(1*s*)
4.50037	0.07048	1412.29	0.004813	2038.41	0.004479	2714.89	0.004324
0.681277	0.40789	206.885	0.037267	301.689	0.034581	415.725	0.032265
0.151374	0.64767	45.8498	0.172403	66.4630	0.164263	91.9805	0.156410
		12.3887	0.459261	17.8081	0.453898	24.4515	0.447813
		3.72337	0.456185	5.30452	0.468979	7.22296	0.481602
		(2*s*)		(2*s*)		(2*s*)	(2*s*)
		0.524194	0.522342	0.764993	0.513598	1.06314	0.504708
		0.163484	0.594186	0.234424	0.605721	0.322679	0.616743
		(2*p*)		(2*p*)		(2*p*)	(2*p*)
		4.18286	0.112194	5.95461	0.119664	7.75579	0.129373
		0.851563	0.466227	1.23293	0.474629	1.62336	0.481269
		0.199206	0.622569	0.286752	0.611142	0.36503	0.604484

Table 2. *Energy comparison (a.u.) with Hartree-Fock calculations*

	Hydrogen (^1S)		Carbon (^3P)		Nitrogen (^4S)		Oxygen (^3P)	
	Present work	Hartree-Fock[a]	Present work	Hartree-Fock[a]	Present work	Hartree-Fock[a]	Present work	Hartree-Fock[a]
E_T	−0.4970	−0.5000	−37.6104	−37.6886	−54.2754	−54.4009	−74.6121	−74.8093
$E1s$	−0.49698	−0.50000	−11.25443	−11.32552	−15.54489	−15.62892	−20.56811	−20.66864
$E2s$			− 0.67695	− 0.70563	− 0.90633	− 0.94523	− 1.19083	− 1.24428
$E2p$			− 0.41311	− 0.43334	− 0.53851	− 0.56753	− 0.58974	− 0.63186

[a] Clementi, E.: Tables of atomic functions, Supplement to IBM Journal of Research and Development **9**, 2 (1965).

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[1] The correct figures should read H(^1S) − 0.4970, C(^3P) − 37.5900, N(^4S) − 54.2485 *a. u.*

are incorrect. The uncontracted atom energies for the present gaussian sets are thus: $H(^1S)$, $C(^3P)$, $N(^4S)$, $O(^3P)$, -0.4998, -37.6560, -54.3390, -74.7000 a.u. respectively. Thus the total energy loss arising from contraction is 0.11 %, and the overall loss relative to the Hartree-Fock limit is 0.23 %. This represents a compromise between precision and reasonable length of computer runs (up to ten hours) for molecules of this size. As will be seen below the experimental trends in the most obvious experimental measurables, photoelectron energy levels, overall dipole moments and heats of formation, are reasonably well reproduced.

Results

a) Total Energies

The geometries used in the computations are the most recent ones for each molecule [10–12] together with the earlier one for pyrrole [13] (cf. Clementi). All of the molecules have C_{2v} symmetry; and the occupied closed shells are $1a_1^2$ to $9a_1^2$, $1b_2^2$ to $6b_2^2$, $1b_1^2$, $2b_1^2$, $1a_2^2$.

For pyrrole, the total energy (Table 3) obtained with the Roos and Siegbahn basis set is apparently marginally better than the Clementi one; however, this really results from the better atom energies, so that the molecular binding energies in both calculations are equal. For both pyrrole and furan about 50 % of the experimental binding energy is accounted for, and this is about the same as is usually obtained with calculations of these types. There is no experimental data for 1,2,5-oxadiazole, but the Table 4 shows the figures for calculated and observed binding energy for a series of 5-membered ring heterocycles. All the calculations use the same contraction procedure; the results of Berthier *et al.* [6] have been corrected for the erronious atom energies used (see above). The experimental (B exp.) and calculated (B theor.) binding energies are linearly related by the relationship $B_{\text{exp}} = 0.7347\ B_{\text{theor}} + 633$ (Kcal/mole) for the five compounds where data is available, with a standard error of 11 Kcal/mole; we note in passing that a very similar relationship ($B_{\text{exp}} = 0.776\ B_{\text{theor}} + 731$ (Kcal/mole)) holds for the azines (see later work). We feel that limited extrapolation is possible at this time; thus the experimental binding energies corresponding to the theoretical figures for 1,2,5-oxadiazole, 4H-1,2,4-triazole (this is not the preferred tautomer in reality) and oxazole are estimated as 755, 802, 857 Kcal/mole respectively.

b) Orbital Energies and Ionisation Potentials

The orbital energies (Table 2) of the 1s, 2s and 2p electrons differ from the Hartree-Fock values for the free atoms by about 1 eV. In the molecules studied (Table 2, 3) it is clear that the orbitals $1a_1$ to $3a_1$, $1b_2$ and $2b_2$ are only slightly perturbed 1s atomic orbital levels; there does appear to be a larger splitting of the "carbon" levels in furan (1.8 eV) than in pyrrole (1.2 eV). Although more delocalised the orbitals $4a_1$ to $6a_1$ and $3b_2$ can still be identified as largely 2s levels. The hydrogen 1s orbitals in contrast are strongly delocalised and are only particularly evident in the highest A_1 and B_2 levels. One particularly notable feature is the $6b_2$ orbital in 1,2,5-oxadiazole which is predominantly the antisymmetric combination

Table 3. *Energies (in a.u.) for the molecules*

	Pyrrole (1)[a]	*Pyrrole (2)*[b]	*Pyrrole (3)*[c]	*Furan*	*1,2,5-Oxadiazole*
Total energy	-208.04264	-208.04241	-207.93135	-227.79358	-259.64308
One electron	-595.83665	-595.25258	[d]	-623.21600	-673.12907
Two electron	226.69231	226.42458	[d]	234.83559	250.27118
Nuclear repulsion	161.10170	160.78558	160.78558	160.58683	163.21480
Atom sum total	-207.20225	-207.20225	-207.09356	-227.04202	-259.37785
"Binding energy"	-0.84039	-0.84016	-0.83779	-0.75156	-0.26523
Orbital energies	A1	A1	A1	A1	A1
	-15.72590	-15.72131	-15.71000	-20.67927	-20.73622
	-11.42840	-11.42939	-11.42520	-11.47535	-15.77459
	-11.38365	-11.38221	-11.37931	-11.41504	-11.49699
	-1.35794	-1.34903	-1.32387	-1.52066	-1.62655
	-1.10288	-1.10121	-1.09548	-1.15807	-1.25085
	-0.84267	-0.84014	-0.82508	-0.83216	-0.91439
	-0.78247	-0.78661	-0.77787	-0.79128	-0.80352
	-0.64962	-0.64916	-0.64759	-0.62334	-0.63299
	-0.58873	-0.58180	-0.57659	-0.58053	-0.56878
	B2	B2	B2	B2	B2
	-11.42871	-11.42969	-11.42526	-11.47578	-15.77483
	-11.38367	-11.38229	-11.37850	-11.41516	-11.49717
	-1.03895	-1.03955	-1.03448	-1.07267	-1.29409
	-0.81694	-0.81058	-0.79702	-0.84447	-0.89784
	-0.63599	-0.63973	-0.62429	-0.66640	-0.69916
	-0.60141	-0.60341	-0.60219	-0.63627	-0.53855
	B1	B1	B1	B1	B1
	-0.64993	-0.64535	-0.63133	-0.69795	-0.75231
	-0.42801	-0.42646	-0.42529	-0.47309	-0.52966
	A2	A2	A2	A2	A2
	-0.38014	-0.38378	-0.38794	-0.41493	-0.50485

[a] Based upon the geometry of Ref. [12] and the gaussian set of Ref. [7].

[b] Based upon the geometry of Ref. [13] and the gaussian set of Ref. [7].

[c] Results of Ref. [5].

[d] Not given in Ref. [5].

Table 4. *Calculated and observed binding energies and heats of formation*

	Pyrrole	*Furan*	*Pyrazole*	*Imidazole*	*Isoxazole*	*Oxazole*	*4H-1,2,4-Triazole*	*1,2,5-Oxadiazole*
SCF binding energy (a.u.)	-0.840	-0.752	-0.568	-0.594	-0.447	-0.485	-0.366	-0.265
Obs. binding energy (a.u.)	-1.640	-1.533	-1.445	-1.465	-1.325	-1.365	-1.275	-1.205
$\Delta H_f^0(g)$ (Kcalmole^{-1})	+31	-8.3	+43	+31	+13	-12	+32	-23

Table 5. *Experimental photoelectron spectra* (eV)

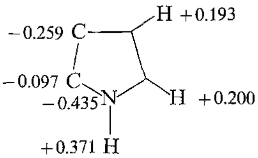
Pyrrole	8.23 (π)	9.22 (π)	12.85	13.65	14.3	14.7	17.5 (π)
Furan	9.08 (π)	10.42 (π)	13.00	13.75	14.30	15.15	17.48 (π)
	19.0	22.8	23.2				
1,2,5-Oxadiazole 11.80 ($2\pi+\sigma$), 12.80, 14.35, 16.3, 17.73 (π).							

of p_x nitrogen orbitals; this is analogous to the classical antisymmetric combination of non-bonding electrons but with lower energy.

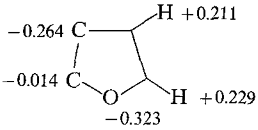
Direct equating of the SCF orbital energies with vertical ionisation potentials obtained by photoelectron spectra is possible (Koopman's Theorem). For molecules where excitation can occur from orbitals of different symmetries, complications arise unless the vibrational fine structure of the photoelectron spectrum can be analysed. For heteroaromatic molecules this is generally not possible except to identify certain π-electron excitations. This has been done in the present work, and the remaining absorptions have been *assumed* to follow the calculated order; when the levels are well spaced this is certainly likely to be true.

The spectra for furan [14] and pyrrole [15] have been reported down to 20 and 10 eV respectively, but there is no reported data for 1,2,5-oxadiazole. We have confirmed and extended (Table 5) the previous observations, particularly in the last case using the known synthetic method [16]. The spectra were obtained down to 21 eV for each molecule with a Perkin-Elmer PS-16 and that for furan was extended to 24 eV with a modified instrument (by arrangement with Perkin-Elmer Ltd.). In the furan and pyrrole spectra the three π-electron excitations are readily identified from the vibrational fine structure (c.f. [14]); as well as these, seven σ-excitations (two not well resolved) are visible for furan and four for pyrrole. The spectrum of the oxadiazole has fewer but more complex excitations and only five distinct absorptions are apparent above 21 eV. However, the very uneven signal intensities of these, in a region (11–15 eV) where the instrument sensitivity is reasonably constant leads us to suppose that the lowest and most intense broad band corresponds to probably three closely spaced bands (including one π level). Since there is at present no clear method of determining the orbital symmetry from which the σ-excitations occurred, we have attempted a correlation in two stages; (a) a preliminary correlation of the π-levels of the three molecules, (b) a least squares fit of all the observed excitations with the orbital energies. In the first case (a) if π_i^M is used to represent the i-th π-ionisation potential of molecule M, where M = P(pyrrole), F(furan) or O(1,2,5-oxadiazole), the observed and calculated order is $\pi_1^P < \pi_1^F < \pi_2^P < \pi_2^F < \pi_1^O < \pi_2^O < \pi_3^P < \pi_3^F < \pi_3^O$. A least squares fit leads to $\pi_{\text{expt}} = 1.0055\,\pi_{\text{calc}} - 2.203$ eV, with a standard error of 0.39 eV. In fact most of the error arises from the uncertainties in placing the 1,2,5-oxadiazole experimental figures and the standard error is reduced to 0.20 eV if the calculation is only based on furan and pyrrole. It is notable that Berthier et al.'s [6] results for isoxazole and pyrrazole can be correlated in the same way with the present work, the first two excitations being compared with the experimental data of Baker *et al.* [15]; the least squares fit is similar $\pi_{\text{expt}} = 1.030\,\pi_{\text{calc}} - 2.436$ eV. This is a very satisfactory fit since the results of Berthier *et al.* were based upon geometries estimated from averaged bond lengths in related compounds.

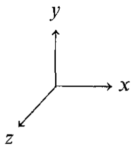
The least squares fit of all the available data for the photoelectron spectra gives the following results: pyrrole (7 points) $IP_{(expt.)} = 1.0088\, IP_{(calc.)} - 2.505$; furan (10 points) $IP_{(expt.)} = 1.199\, IP_{(calc.)} - 5.58$; 1,2,5-oxadiazole (5 points) $IP_{(expt.)} = 1.120\, IP_{(calc.)} - 4.32$ eV. In all of these cases the line is much improved if only the first few ionisation potentials are included as in the first series of correlations, and a slope of unity should be obtained; the intercept represents the error due to small basis set, correlation energy and errors arising from Koopman's Theorem. On this last point Clementi [17] has shown that the difference in total energy between pyridine and the $^2A_2$ positive ion is 0.42486 a.u. (11.46 eV) whereas Koopman's Theorem applied to the neutral molecule gives an ionisation potential of 0.44725 a.u. (12.17 eV); similar considerations apply with the present work and these will be reported at a later date, as will work with a more extended basis.

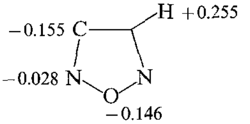


$\mu_{calc.} = 2.49$ D[b]
$\mu_{calc.} = 2.30$ D[c]
$\mu_{exptl.} = 1.80$ D [11]



$\mu_{calc.} = -0.64$ D
$\mu_{exptl.} = -0.67$ D [10]





$\mu_{calc.} = -2.96$ D
$\mu_{exptl.} = -3.38$ D [13]

Fig. 1. Dipole moments[a] and charge distributions

[a] A positive dipole moment has its negative end pointing in a positive Cartesian direction.
[b] Using the geometry of Ref. [12].
[c] Using the geometry of Ref. [13].

c) Dipole Moments and Electron Distribution

The dipole moments and net atomic charges were calculated from a Mulliken population analysis and are shown in Fig. 1. In all of these molecules the α-carbon or nitrogen atoms are nearly electrically neutral and the resultant dipole moment arises from the partial cancellation of the charges at the 1- and 3,4-positions (for furan and the oxadiazole) and from the N–H dipole for pyrrole. Using Clementi's eigenvectors and geometry [13] we obtained a dipole moment of 2.30 D, identical with the figure obtained with this geometry and the present gaussian set. However, these figures are somewhat fortuitous since the more recent geometry, which is apparently an improvement from total energy considerations, leads to a poorer dipole moment (2.49 D). Clearly the exponents used for hydrogen and nitrogen are critical in this evaluation; the incorporation of polarisation functions on the hydrogen atoms leads to a substantial improvement (see next paper). The dipole moment for furan is in excellent agreement with experiment and we were unable to improve upon it by the addition of polarisation orbitals on any or *all* atoms. The oxadiazole result is in fair agreement with experiment, and this was dramatically improved by polarisation functions.

A feature of ab initio calculations using contracted bases of these types is the nearly constant C–H dipole, with the hydrogen atom having a charge near +0.2 e. This can lead to carbon atoms in calculations of some azines having a higher negative charge than the nitrogen atoms, and this seems improbable at first sight. It is clear that part of this effect is a result of the use of very limited basis sets (for example, see Ref. [18]) and part is a result of the equipartition of the overlap populations in the Mulliken analysis. Our following paper explores the use of polarisation functions to avoid the former problem.

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